

## *Interplay Between Electronic and Geometric Structures at Surfaces*

**D**eep within an ideal crystalline solid, every atom has a full complement of neighboring atoms, held in place by chemical bonds in all three dimensions. In contrast, atoms on the two-dimensional surface remain partially unattached, leaving “unsaturated” bonds that are available for chemical reactions with external substances. An understanding of how simple molecules bond to such surfaces is important for many different fields of science, including heterogeneous catalysis, electrochemistry, biomaterials, and molecular environmental science. A basic question is why molecules preferentially bond to sites with a particular geometry. At Beamline 8.0.1 of the ALS, a research group from Sweden has employed x-ray emission spectroscopy experiments on carbon monoxide and performed ab initio electron density calculations to explore the subtle interplay between the electronic and geometric structure of adsorbates.

Carbon monoxide (CO) is known for its ability to populate different adsorption sites, depending on the

substrate, CO coverage, temperature, and influence from coadsorbate species. In this work, the researchers compared the electronic bond structure of CO adsorbed onto a nickel substrate in three different geometries. The objective was to study how the electronic structure of the CO changes when it is brought into direct contact with one, two, and four atoms at the surface (i.e., with increasing coordination with the substrate atoms).

The electronic structure of the CO-nickel complex results from the mixing of the CO electron orbitals with those of the nickel substrate. This hybridization creates new orbitals that can be characterized as having either  $\pi$  or  $\sigma$  symmetry, depending on the shape of the resulting orbitals' electron distribution. A study of how electrons are shared and redistributed upon adsorption of a molecule at different sites requires an experimental method that allows the determination of atom- and symmetry-specific electronic structures. Furthermore, the information from the small

number of adsorbed molecules must be separated from the information from the huge number of substrate atoms.

At ALS Beamline 8.0.1, atom-specific valence electrons can be selectively probed using x-ray emission spectroscopy: only the valence electrons in proximity to the core hole localized on either the carbon or oxygen atom participate in the x-ray decay process. Also, by varying the detection angle of the x rays emitted upon decay, the researchers can distinguish between electron states of  $\pi$  and  $\sigma$  symmetry. The resulting carbon and oxygen K-edge spectra show, most notably, a strong adsorption-induced band ( $d_\pi$ ) and different CO molecular states, both with significant intensity variations. To compare the experimental results with theory, orbital contour plots were generated based on ab initio electron density calculations (using density functional theory). Analysis shows that the  $\sigma$  interaction is repulsive while the  $\pi$  interaction is attractive and also weakens the internal CO bond. Both

the  $\pi$  and  $\sigma$  interactions increase with higher coordination, but the two contributions partly compensate for each other.

With this information, we can better understand the rich chemistry of CO adsorbed on metals and the variety of behaviors arising from the different possible adsorption sites. The small differences in adsorption energies previously observed for the different sites had been interpreted as an indication of rather similar bonding. In addition, it was known from vibrational spectroscopy that the CO stretch frequency decreases with increasing coordination to the substrate. Based on the findings reported here, such phenomena can be understood in terms of the interplay between the  $\pi$  and  $\sigma$  interactions. The  $\pi$  interaction weakens the internal CO bond, decreasing the CO stretch frequency as coordination increases, and the balance between  $\pi$  bonding and  $\sigma$  repulsion leads to small differences in adsorption energies despite very large differences in electronic structure. ■

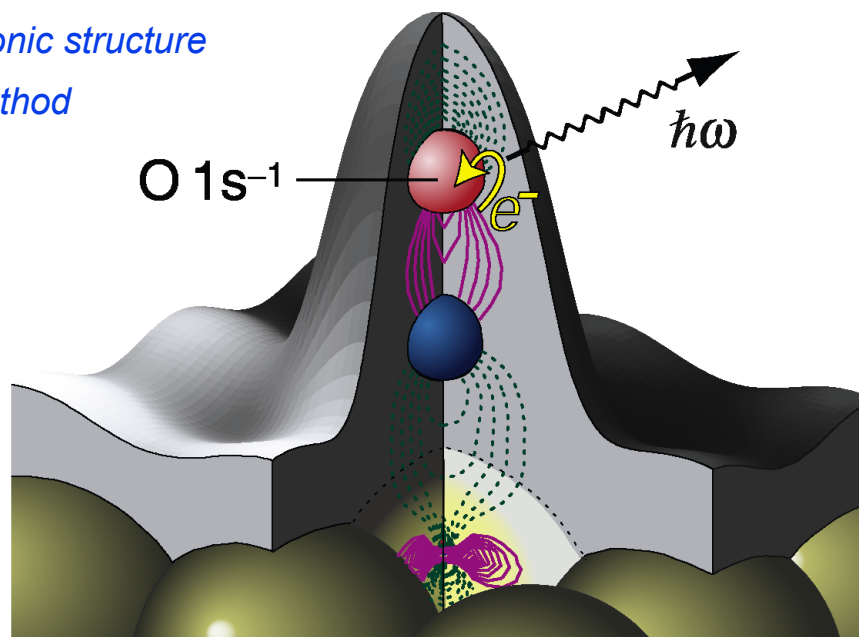
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A. Föhlisch, M. Nyberg, J. Hasselström, O. Karis, L.G.M. Pettersson, A. Nilsson, “How Carbon Monoxide Adsorbs in Different Sites,” *Phys. Rev. Lett.* **85**(15), 3309 (2000).

# HOW CARBON MONOXIDE ADSORBS AT DIFFERENT SITES

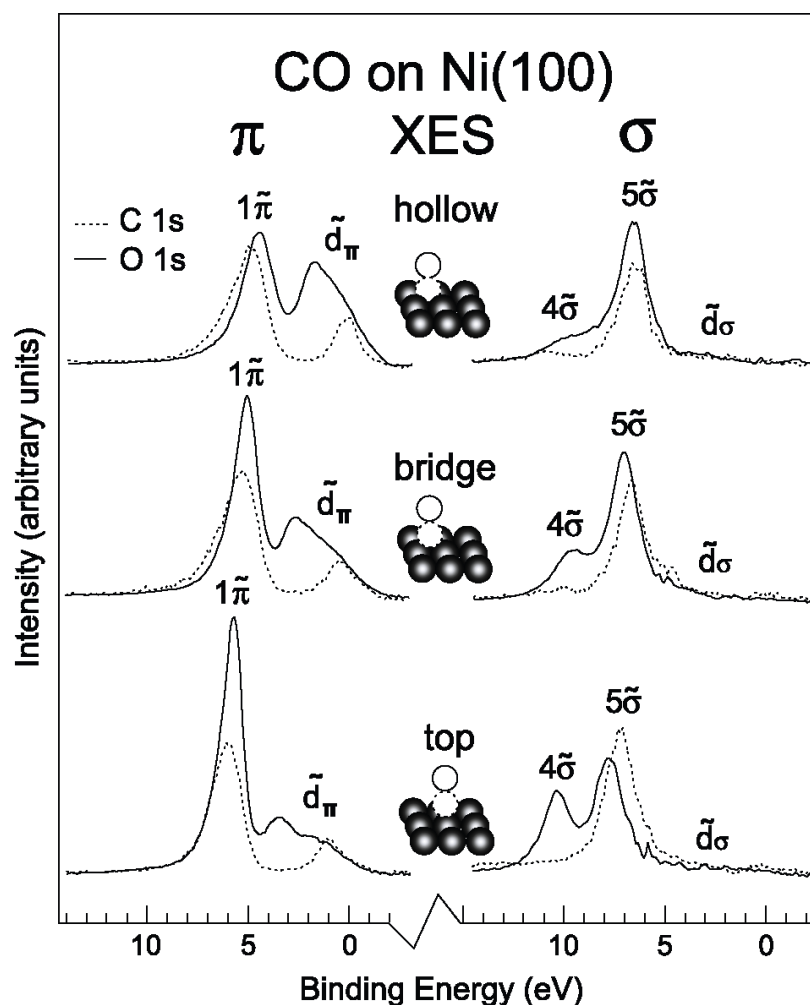
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- Why do molecules preferentially bond to sites with a particular geometry? Answer(s) relevant to heterogeneous catalysis, electrochemistry, biomaterials, molecular environmental science, etc.
- CO/Ni – prototypical adsorbate
  - Effect of increasing coordination on electronic structure
  - Requires atom- and symmetry-specific method
- ALS Beamline 8.0.1
  - X-ray emission spectroscopy
  - Valence electrons selectively probed
  - Vary detection angle of x-ray emission
  - Distinguish between  $\pi$  and  $\sigma$  interactions



# HOW CARBON MONOXIDE ADSORBS AT DIFFERENT SITES

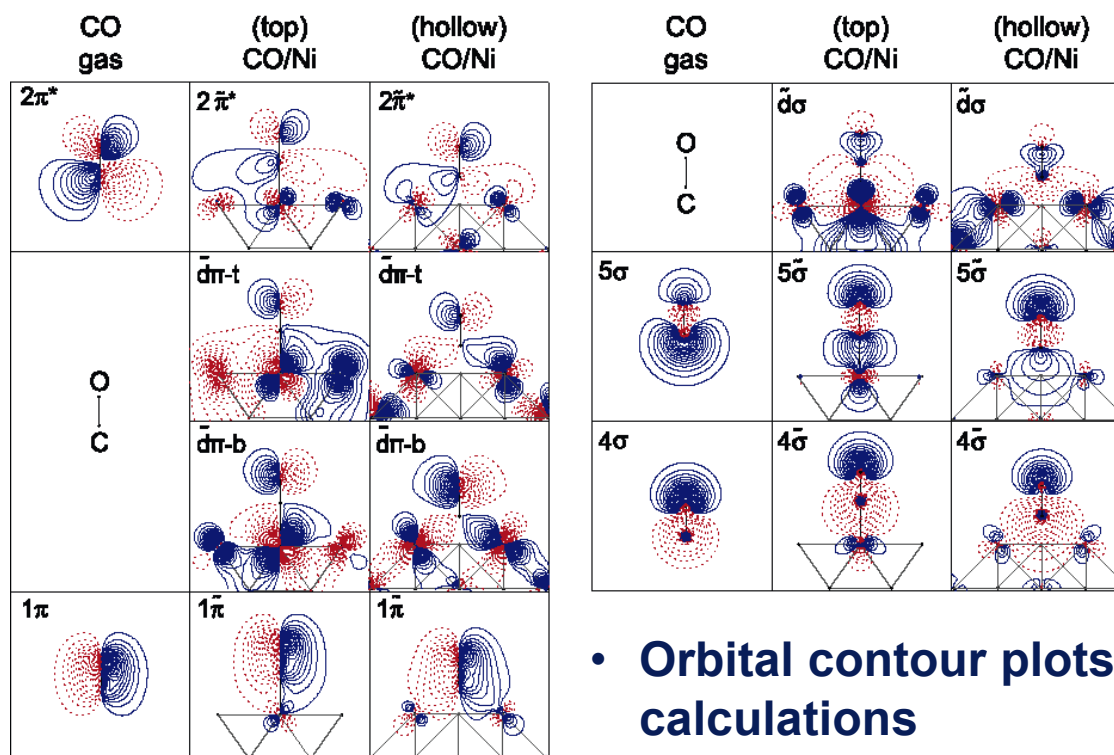
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*C and O K-edge spectra of CO adsorbed on Ni(100). Energy scale is relative to the Fermi level.*

# HOW CARBON MONOXIDE ADSORBS AT DIFFERENT SITES

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- **Orbital contour plots from ab initio calculations**

- $\sigma$  interaction is repulsive
- $\pi$  interaction is attractive, weakens internal CO bond
- Both interactions increase with higher coordination
- Small differences in absorption energies despite large differences in electronic structure